ECS Transactions, 3 (35) 493-502 (2007)
10.1149/1.2798692, copyright The Electrochemical Society

Behaviour of Rare Earth Elements in Molten Salts in Relation to Pyrochemical Reprocessing of Spent Nuclear Fuels

V. A. Volkovich[a], B. D. Vasin[a], T. R. Griffiths[b], I. B. Polovov[a], E. O. Medvedev[a], and S. M. Yakimov[a]

[a] Department of Rare Metals, Ural State Technical University-UPI, Ekaterinburg 620002, Russia
[b] Redston Trevor Consulting, Ltd., Leeds LS17 8RF, UK

The kinetics of chlorination of lanthanide oxides (by Cl_2 and HCl) and precipitation of lanthanide phosphates was studied by *in situ* electronic absorption spectroscopy in 3LiCl-2KCl and NaCl-KCl melts at 400-750 ^oC. Products of the chlorination are the corresponding hexachlorospecies, $LnCl_6^{3-}$, and the rate of chlorination increases with increasing temperature. Composition of the precipitated phosphates depends on the melt composition and 1.5-5 fold excess of phosphate, depending on the nature of lanthanide, is needed for the complete removal of the lanthanides from the melt. Over three hours are required for completing the reaction of phosphate precipitation.

Introduction

Pyrochemical reprocessing of spent nuclear fuels in high temperature alkali halide melts is one of the prospective alternatives to the modern day extraction technologies. Several technologies have been suggested over the past years with two of them reaching a pilot plant scale, *i.e.*, reprocessing metallic fuel developed at Argonne National Laboratory in the USA and ceramic oxide fuel at Research Institute of Atomic Reactors in Russia. In ceramic fuels yttrium and lanthanide (La to Dy) fission products form oxide phases (1, 2). Lanthanide oxides can be dissolved in a molten chloride salt bath by reacting them with a suitable gaseous chlorinating agent.

After the spent fuel (either ceramic oxide or metallic) is dissolved in the melt and noble fission products, uranium, plutonium and some other actinides are removed, the melt needs to be cleansed from the remaining fission elements and corrosion products, before it can be reused. Precipitation of fission product elements as phosphates offers an attractive solution. Most of the inorganic phosphates are insoluble in chloride melts and thus these precipitates can easily be separated from liquid melts. Separating wastes in phosphate form is also very convenient for future vitrification, since they form stable non-leachable glasses, and phosphates themselves are very stable in highly radioactive environments. Optimizing processes of phosphate precipitation requires detailed knowledge of the reactions involved.

Precipitation of phosphates from molten salts has been previously reported for NaCl, KCl and NaCl-KCl based melts. The elements studied included uranium (3, 4), plutonium (5, 6), americium and curium (7), and a few lanthanides (3). Sodium or potassium orthophosphates were employed as precipitants. For trivalent actinides and lanthanides the reactions resulted in the formation of double phosphates of composition

$M_3Me_2(PO_4)_3$, M = Na or K, Me = Ce, Pr, Nd, Sm, Eu, Gd, Pu, Am or Cm. In the case of uranium, formation of $NaUO_2PO_4$ and $NaU_2(PO_4)_3$ was reported in U(VI) and U(IV) containing melts, respectively. We have previously investigated the effect of temperature, melt composition and the nature of phosphate precipitant employed (ortho-, meta- or pyrophosphate) on the composition and particle size of lanthanide phosphates (from La to Dy) precipitated from 3LiCl-2KCl and NaCl-KCl melts (8-10). Reactions in NaCl-KCl melts produce double phosphates, $Na_3Ln_2(PO_4)_3$ or $Na_3Ln(PO_4)_2$; only single orthophosphates, $LnPO_4$, can be formed in 3LiCl-2KCl melts, the excess of added alkali phosphate reacts with lithium ions forming sparingly soluble Li_3PO_4.

Here we report the results of our recent studies on kinetics of dissolution of lanthanide oxides by chlorinating them in a molten salt bath employing either chlorine or hydrogen chloride as chlorinating agents. In the second part of the work we investigated precipitation of rare earth phosphates aiming to determine the optimal conditions for the complete removal of Ln(III) ions from alkali chloride based melts.

Experimental

The experiments were performed in the melts based on 3LiCl-2KCl eutectic or NaCl-KCl equimolar mixture between 400 and 750 ^oC. Lanthanide oxides were introduced into the melt and dissolved by bubbling gaseous chlorine or hydrogen chloride through. The experiments were performed in standard 1-cm path length optical silica cells and the progress of the reaction was followed by measuring the electronic absorption spectra of the melts. The experimental set-up for high temperature spectroscopy measurements based on Ocean Optics SD2000 fibre optic spectrometer was described previously (11). Chlorine was prepared by electrolysis of molten lead chloride, hydrogen chloride by acting concentrated sulphuric acid onto sodium chloride. After each experiment a sample of the melt was withdrawn into a silica capillary tube using a syringe, quenched and the concentration of lanthanide ions was determined spectrophotometrically using Arsenazo I (12).

The experiments on phosphate precipitation were conducted under an argon atmosphere either in spectroscopy cells (to monitor the progress of the reaction) or in alumina crucibles (for the bulk studies). Melts containing yttrium and lanthanide chlorides were prepared by chlorinating corresponding oxides by Cl_2 directly in the melt. Sodium and lithium phosphates, Na_3PO_4 and Li_3PO_4, were used as precipitants.

Results and discussion

Reaction of lanthanide oxides with chlorine and hydrogen chloride

When studying chlorination of rare earth oxides the extent of the reaction was followed by *in situ* spectroscopy measurements of Ln(III) concentration in the melt and the examples of the spectra recorded for praseodymium and neodymium are presented in Figs. 1 and 2. Spectral profiles measured during chlorination did not change, and corresponded to the spectra of hexachlorocoordinated species of trivalent lanthanides, $LnCl_6^{3-}$.

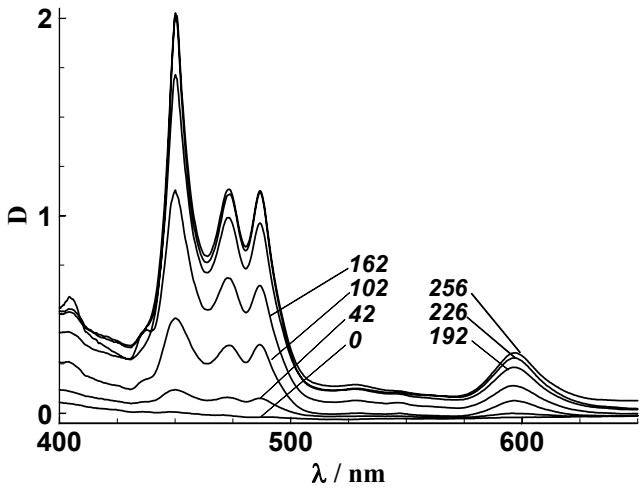

Figure 1. Spectra recorded during reacting Pr_6O_{11} with Cl_2 in 3LiCl-2KCl melt at 400 ^oC (time of reaction in min is given for each spectrum).

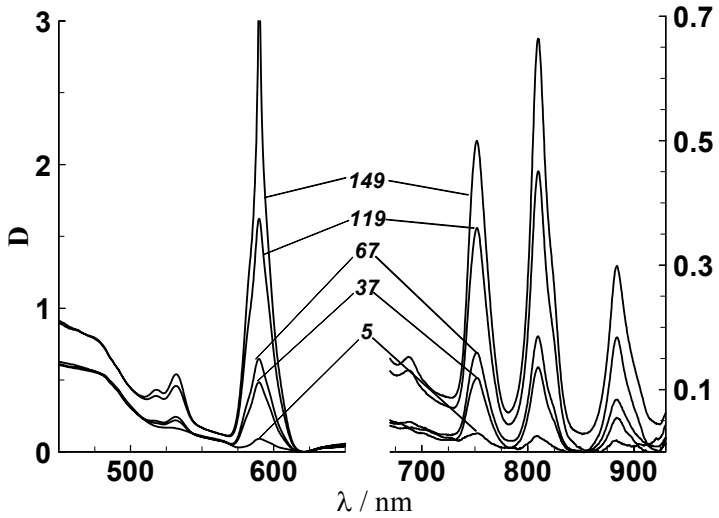

Figure 2. Spectra recorded during reacting Nd_2O_3 with Cl_2 in 3LiCl-2KCl melt at 400 ^oC (time of reaction in min is given for each spectrum).

During the reaction of Pr_6O_{11} with Cl_2 in NaCl-KCl melt, the melt was regularly visually inspected and after 10 min of chlorination the precipitate on the bottom of the cell was black, indicating unreacted Pr_6O_{11}. However, after 10 more minutes a layer of light green precipitate was seen on the top of the Pr_6O_{11}; the proportion of this precipitate increased with time and that of the black phase decreased until only the light green precipitate was present which finally completely dissolved on further chlorination. The formation of this precipitate indicates that the reaction of chlorine with Pr_6O_{11} occurs (at least partially) in two stages, *via* the intermediate formation of a an insoluble in the melt light-green compound. Quite likely this is praseodymium(III) oxychloride, which is known to be green. Lanthanide oxychlorides are insoluble in chloride melts and the second stage of the reaction in this case is the chlorination of the oxychloride formed. ΔG of the conversion of a lanthanide oxide into a trichloride or an oxychloride are very close but they considerably greater (in absolute values) than that of chlorination of the oxychloride into the corresponding trichloride. Thus it is quite likely that during

chlorination of lanthanide oxides using chlorine gas initial products formed are soluble chloride and insoluble oxychloride, the latter being subsequently converted into chloride. Determination of the rate determining step of this heterogeneous chlorination reaction requires performing kinetic studies.

Ultimately lanthanide oxides react with chlorine or hydrogen chloride in molten alkali metal chlorides producing corresponding lanthanide trichlorides, that dissolve in the melts forming $LnCl_6^{3-}$ complex ions. The following reactions are proposed for chlorination using Cl_2:

$$Ln_2O_3 + 3\ Cl_2 + 6\ Cl^- \rightarrow 2\ LnCl_6^{3-} + {}^3/_2\ O_2 \quad [1]$$
$$Pr_6O_{11} + 9\ Cl_2 + 18\ Cl^- \rightarrow 6\ PrCl_6^{3-} + {}^{11}/_2\ O_2 \quad [2]$$
$$Tb_4O_7 + 6\ Cl_2 + 12\ Cl^- \rightarrow 4\ TbCl_6^{3-} + {}^7/_2\ O_2 \quad [3]$$

The concentration of Ln(III) ions in the melt gradually and initially essentially linearly increased over time, Figs. 3 and 4, and the rate of the chlorination increased with temperature, Fig. 3. Similar linear increase of Ln(III) concentration in the melt has been previously observed when studying reaction of metallic neodymium and praseodymium with HCl in NaCl-2CsCl eutectic at 550-750 ^oC (13). With the course of time (as the lanthanide oxide is being used up and its surface area decreases) the rate of formation of lanthanide chloride slows down and the concentration of Ln(III) levels up, Fig 4.

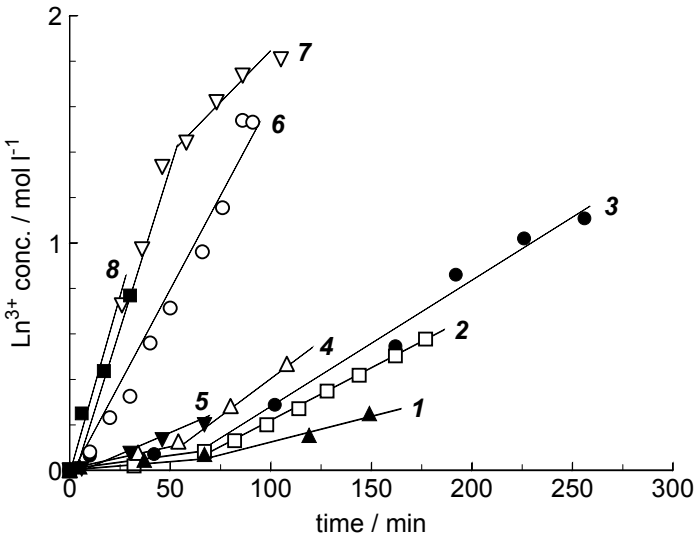

Figure 3. Kinetics of chlorination of lanthanide oxides by Cl_2 in alkali chloride melts. 1 - Nd_2O_3 in 3LiCl-2KCl at 400 ^oC; 2 - Nd_2O_3 in 3LiCl-2KCl at 550 ^oC; 3 - Pr_6O_{11} in 3LiCl-2KCl at 400 ^oC; 4 - Pr_6O_{11} in 3LiCl-2KCl at 550 ^oC; 5 - Nd_2O_3 in NaCl-KCl at 750 ^oC; 6 - Pr_6O_{11} in NaCl-KCl at 700 ^oC; 7 - Sm_2O_3 in NaCl-KCl at 700 ^oC; 8 - Tb_4O_7 in NaCl-KCl at 700 ^oC.

Preparation of the melts containing 1-2 mol dm^{-3} of $LnCl_6^{3-}$ (or 8-15 wt.% of a corresponding Ln) requires from one to three hours depending on the cationic melt composition and the temperature. The rate of the chlorination of rare earth oxides by chlorine in molten salts (calculated with the correction for the initial relative amount of the solid oxide added into the melt, Table I) does not depend much on the nature of the oxide. Oxides of trivalent lanthanides, Ln_2O_3, also react with hydrogen chloride with

approximately the same rate, Table II, but the reaction of mixed Ln(III,IV) oxides, Pr_6O_{11} and Tb_4O_7, proceeds somewhat faster. The results obtained under various conditions are summarised in Tables I and II for Cl_2 and HCl, respectively. The reactions of studied rare earth oxides with Cl_2 or HCl in alkali chloride melts are of zero order in respect to the lanthanide chlorides formed.

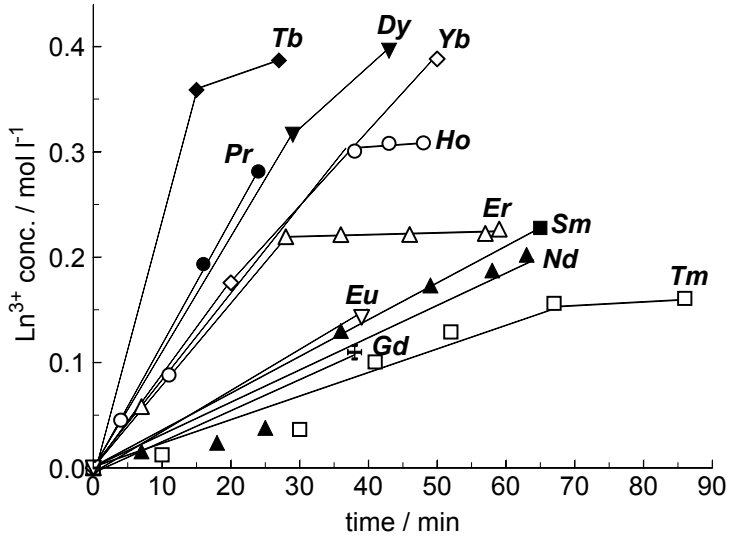

Figure 4. Kinetics of chlorination of lanthanide oxides by HCl in NaCl-KCl melts at 750 °C, symbols of the corresponding element is given for each line.

TABLE I. Reaction of lanthanide oxides with Cl_2 in 3LiCl-2KCl and NaCl-KCl based melts.

Ln oxide	Melt	T, °C	m(oxide)/ m(salt)	Final Ln conc., mol/l	Time of reaction, min	Average chlorination rate, mol/h	Mean chlorination rate*, mol/h
Pr_6O_{11}	3LiCl-2KCl	400	0.081	0.997	256	0.0009	0.011
Pr_6O_{11}	3LiCl-2KCl	550	0.069	0.512	146	0.0010	0.015
Pr_6O_{11}	NaCl-KCl	705	0.270	1.540	91	0.0082	0.030
Pr_6O_{11}	NaCl-KCl	750	0.025	0.227	68	0.0010	0.040
Pr_6O_{11}	NaCl-KCl	750	0.057	0.521	70	0.0020	0.035
Nd_2O_3	3LiCl-2KCl	400	0.060	0.212	149	0.0003	0.004
Nd_2O_3	3LiCl-2KCl	550	0.117	0.577	177	0.0014	0.012
Nd_2O_3	NaCl-KCl	750	0.021	0.157	83	0.0007	0.033
Sm_2O_3	3LiCl-2KCl	550	0.048	0.400	215	0.0006	0.012
Sm_2O_3	NaCl-KCl	700	0.308	1.808	105	0.0075	0.024
Tb_4O_7	NaCl-KCl	700	0.090	0.769	71	0.0033	0.036

* Mean chlorination rate was calculated as the ratio of the average chlorination rate to initial specific content of Ln oxide in the melt (m(oxide)/m(salt)).

Comparison of the data presented in Tables I and II (taking into account the initial solid oxide to liquid melt ratio) shows that generally hydrogen chloride is a better chlorinating agent for lanthanide oxides than chlorine (although the thermodynamic calculations indicate the opposite). This can be explained by higher solubility and higher diffusion coefficients of HCl, compared to Cl_2, in fused alkali chlorides (14, 15). Rare earth oxides thus react primarily with the chlorinating agent dissolved in an alkali chloride melt.

TABLE II. Reaction of lanthanide oxides with HCl in NaCl-KCl based melts at 750 °C.

Ln oxide	m(oxide)/ m(salt)	Final Ln conc., mol/l	Time of reaction, min	Average chlorination rate, mol/h	Mean chlorination rate*, mol/h
Pr_6O_{11}	0.0448	0.2813	24	0.0238	0.0759
Nd_2O_3	0.0439	0.2023	63	0.0029	0.0326
Sm_2O_3	0.2711	0.2277	65	0.0166	0.0270
Eu_2O_3	0.0995	0.1430	39	0.0101	0.0415
Gd_2O_3	0.0631	0.1098	38	0.0063	0.0427
Tb_4O_7	0.1309	0.3867	27	0.0366	0.0626
Dy_2O_3	0.1259	0.3960	43	0.0110	0.0385
Ho_2O_3	0.0835	0.3084	48	0.0063	0.0334
Er_2O_3	0.0743	0.2268	59	0.0045	0.0266
Tm_2O_3	0.0484	0.1608	86	0.0020	0.0194
Yb_2O_3	0.1307	0.3882	50	0.0091	0.0319

* See note to Table I.

Precipitation of lanthanide phosphates

Reaction of lanthanide chlorides in chloride melts with alkali phosphates can result in the precipitation of simple and double phosphates (9, 10). To determine time required for completing reaction the course of precipitation was followed spectroscopically. The results obtained for neodymium in 3LiCl-2KCl melts at 550 °C are presented in Figs. 5 and 6 for Na_3PO_4 and Li_3PO_4 precipitants, respectively. In both cases the reaction is fastest in the first 20-40 minutes after adding alkali phosphate and then it gradually slows down. Two to three hours are required to complete the reaction. This is due to relatively low (especially for Li_3PO_4) solubility and slow dissolution rate of alkali metal phosphates in alkali chloride melts. Upon addition of solid sodium or lithium phosphates into the melt a layer of insoluble rare earth phosphate is formed on the surface of alkali phosphate particles that in turn slows down the rate of rare earth phosphate formation/precipitation. Although simple $NdPO_4$ is formed in 3LiCl-2KCl melts, PO_4^{3-}-to-Nd^{3+} mole ration of at least three is required for complete removal of neodymium from 3LiCl-2KCl melt. Comparison of Figs. 5 and 6 shows that at low PO_4^{3-}-to-Nd^{3+} mole ratios (0.5-2) lithium phosphate appears to be somewhat more effective precipitant than sodium phosphate. This might be due to initial reaction of added Na_3PO_4 with Li^+ ions, more abundant than Nd(III) in 3LiCl-2KCl melt, and the phosphate added is partially used up to form sparingly soluble Li_3PO_4. Plotting the obtained data in $\lg C_{Nd}$ - $\lg(\Delta C_{Nd}/\Delta\tau)$ coordinates showed that the precipitation reaction is of the first order in respect to neodymium(III). The rate constant of neodymium precipitation reaction at the mole ratio PO_4^{3-}-to-Nd^{3+} = 3 was 0.021 min^{-1}.

The completeness of rare earths removal from the melt depends on the amount of added phosphate. A series of experiments was conducted on precipitating trivalent Y, La, Ce, Pr, Nd, Sm, Eu and Gd from NaCl-KCl melts at 750 °C using various amounts of added anhydrous Na_3PO_4. Initial PO_4^{3-}-to-Ln^{3+} mole ratios varied from 0.1 to 10. After addition of the phosphate the reaction was allowed to proceed for three hours, the melt then was rapidly quenched and analyzed for the amount of unreacted Ln(III).

Kryukova *et al*. (3) reported that complete removal of lanthanides from NaCl, KCl and NaCl-KCl melts requires a ten fold molar excess of sodium or potassium phosphate. They however did not report the results of experiments (if any were conducted) with lower excess of the added phosphate. Volkovich *et al*. (9, 10) found that over 90-98%

lanthanide precipitation from 3LiCl-2KCl and NaCl-KCl based melts can be achieved using five fold excess of an alkali phosphate. Harrison and Jackson (16) recently reported that three fold excess of phosphate is sufficient for complete precipitation of neodymium from 3LiCl-2KCl melt.

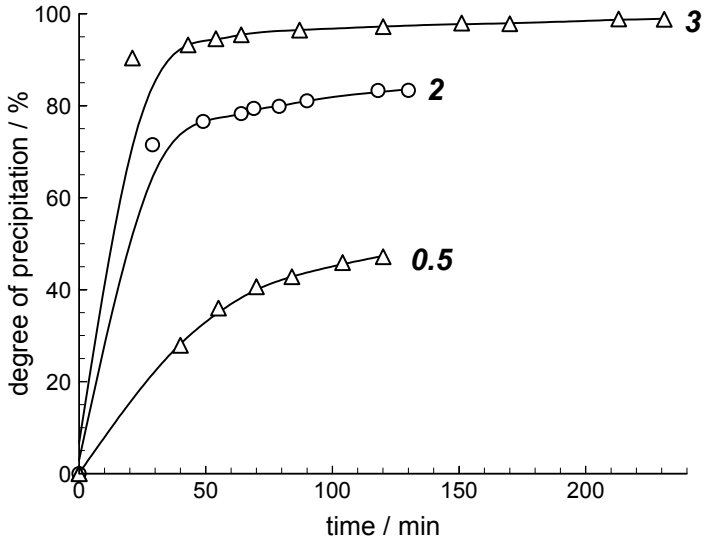

Figure 5. Kinetics of neodymium phosphate precipitation from 3LiCl-2KCl melts by Na_3PO_4 at 550 ^oC and various initial PO_4^{3-} : Nd^{3+} mole ratios (shown for each plot).

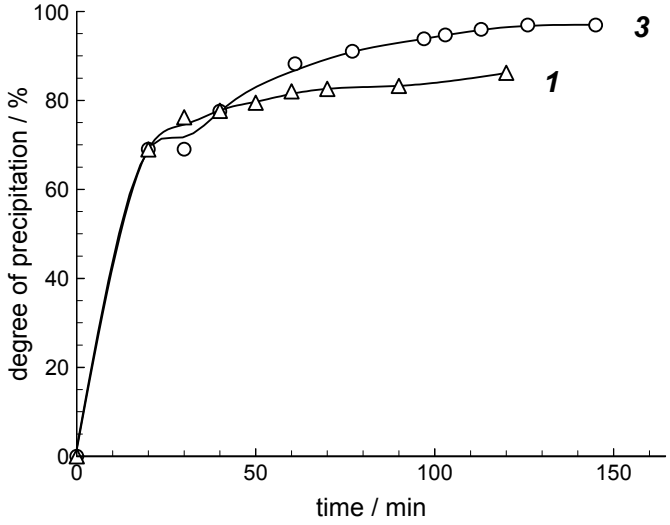

Figure 6. Kinetics of neodymium phosphate precipitation from 3LiCl-2KCl melts by Li_3PO_4 at 550 ^oC and two initial PO_4^{3-} : Nd^{3+} mole ratios (shown for each plot).

The results of systematic experiments conducted in the present work in NaCl-KCl based melts are presented in Fig. 7. Up to five fold excess of the phosphate might be required for complete conversion of rare earth ions into insoluble phosphates. This excess however depends on the nature of lanthanide, greatest excess (around five fold) is needed for precipitation of cerium and praseodymium; lanthanum can be essentially quantitatively precipitated at two-to-four fold excess of the added phosphate. Remaining

studied lanthanides, yttrium, neodymium, samarium, europium and gadolinium, can be converted into insoluble phosphates at PO_4^{3-} : Ln^{3+} mole ratio of 1.5-2.

The composition of lanthanide phosphates precipitated from NaCl-KCl melts depends on the amount of added phosphate precursor. Normal orthophosphates are formed at low PO_4^{3-} : Ln^{3+} mole ratios, increasing this ratio results in precipitation of double alkali metal-lanthanide phosphates, and the following reactions can be suggested:

$$LnCl_6^{3-} + PO_4^{3-} \rightarrow LnPO_4 + 6\ Cl^- \quad [4]$$

$$2\ LnCl_6^{3-} + 3\ PO_4^{3-} + 3\ Na^+ \rightarrow Na_3Ln_2(PO_4)_3 + 12\ Cl^- \quad [5]$$

$$LnCl_6^{3-} + 2\ PO_4^{3-} + 3\ Na^+ \rightarrow Na_3Ln(PO_4)_2 + 6\ Cl^- \quad [6]$$

From the data presented in Fig. 7 it can be concluded that from all the studied rare earth metals only yttrium can be essentially completely precipitated as a simple orthophosphate, YPO_4, since at PO_4^{3-} : Y^{3+} mole ratio around one less than 1 % of yttrium remains in soluble form in the melt.

Quantitative precipitation of lanthanum, cerium and praseodymium is most likely possible only in the form of double phosphates, $Na_3Ln_2(PO_4)_3$ and $Na_3Ln(PO_4)_2$; and $Na_3Ln(PO_4)_2$ is a predominant form in the mixture since complete precipitation of these metals takes place at PO_4^{3-} : Ln^{3+} mole ratios of well above two.

Addition of a five fold excess of Na_3PO_4 into NaCl-KCl-$LnCl_3$ (Ln = Sm, Eu, Gd) melts results in precipitation of $LnPO_4$ and $Na_3Ln(PO_4)_2$ mixtures (9, 10). Only when Ln = Nd the precipitate mainly consists of $Na_3Nd_2(PO_4)_3$ (9). We here found that neodymium, samarium, europium and gadolinium can be completely precipitated from the melt at 1.5-2 fold molar excess of added sodium phosphate and this fact agrees well with the formation of $Na_3Ln_2(PO_4)_3$ or a mixture of $LnPO_4$ and $Na_3Ln(PO_4)_2$.

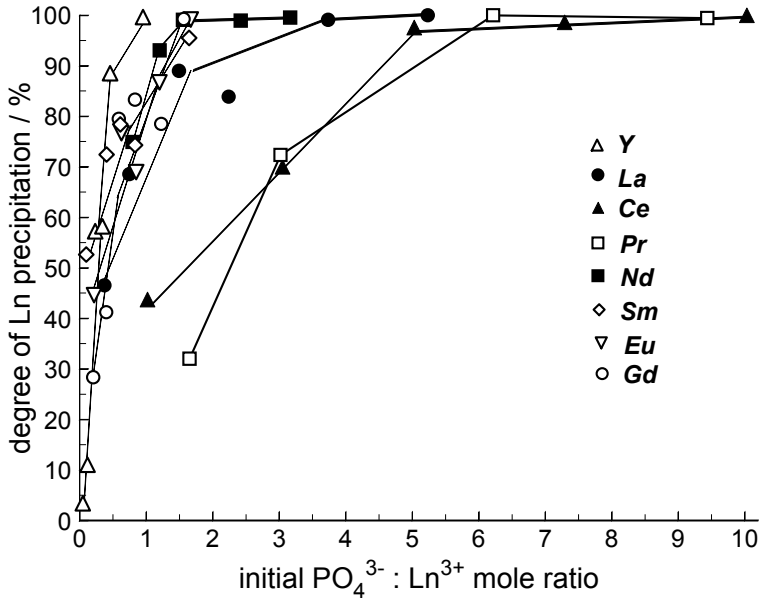

Figure 7. The effect of initial rare earth metal to sodium phosphate mole ratio on extent of removal of rare earth ions from NaCl-KCl melts at 750 ^oC.

Conclusions

Reaction with chlorine or hydrogen chloride in alkali chloride melts can be effectively used for dissolving rare earth oxides and preparing rare earth chloride containing melts. Solid oxide reacts with the chlorinating agent dissolved in the melt and the reaction with HCl proceeds faster than with Cl_2 due to higher solubility and diffusion coefficients of hydrogen chloride in fused alkali chlorides. Depending on the oxide, temperature and cationic melt composition one to three hours are needed for preparing 1-2 mol l^{-1} solution of $LnCl_6^{3-}$, *i.e.*, containing 10-15 wt.% of the corresponding lanthanide in the melt.

Phosphate precipitation has the potential for removing rare earth fission product elements from molten salt solutions arising from pyrochemical reprocessing of spent nuclear fuels. Complete removal of trivalent yttrium and lanthanide species from chloride melts requires addition of excess of the phosphate, varying from 1-1.5 moles of PO_4^{3-} to 1 mole of Ln^{3+} for Y, Eu and Gd to over 5 for La and Ce. Spectroscopic measurements showed that over three hours are needed for the reaction to go to completion.

Acknowledgments

V.A.V., T.R.G. and I.B.P. thank the Electrochemical Society, Inc., for financial assistance making possible presenting this work at 210-th Meeting of the Society.

References

1. H. Kleykamp, *J. Nucl. Mater*., **131,** 221 (1985).
2. H. Kleykamp, *Nucl. Technol*., **80**, 412 (1988).
3. A. I. Kryukova, I. A. Korshunov, V. A. Mitrofanova, A. A. Burnaeva, O. V. Skiba, G. N. Kazantsev and V. T. Sergeeva, in: *Phys. Chem. Electrochem. Molten and Solid Electrolytes*, pt. 1, p. 138, Akad Nauk SSSR, Ural. Nauch. Tsentr, Sverdlovsk (1979) (in Russian).
4. A. I. Kryukova, I. A. Korshunov, A. A. Burnaeva, O. V. Skiba and G. N. Kazantsev, *Sov. Radiochem*. **23**, 106 (1981).
5. A. A. Burnaeva, A. I. Kryukova, G. N. Kazantsev, O. V. Skiba and I. A. Korshunov, *Sov. Radiochem*., **26**, 229 (1984).
6. A. A.Burnaeva, Y. F. Volkov and A. I. Kryukova, *Radiokhimiya*, **36**, 289 (1994).
7. G. N. Kazantsev, O. V. Skiba, A. A. Burnaeva, V. P. Kolesnikov, Y. F. Volkov, A. I. Kryukova and I. A. Koshunov, *Sov. Radiochem*., **24**, 78 (1982).
8. V. A. Volkovich, T. R. Griffiths and R. C. Thied, in *Molten Salts XIII*, H. C. Delong, R. W. Bradshaw, M. Matsunaga, G. R. Stafford and P. C. Trulove, Editors, PV 2002-19, p. 590, The Electrochemical Society Proceedings Series, Pennington, NJ (2002).
9. V. A. Volkovich, T. R. Griffiths and R. C. Thied, *Phys. Chem. Chem. Phys*., **5**, 3053 (2003).
10. V. A. Volkovich, T. R. Griffiths and R. C. Thied, *J. Nucl. Mater.*, **323**, 49 (2003).
11. V. A. Volkovich, , I. May, J. M. Charnock and B. Lewin, *Phys. Chem. Chem. Phys*., **4**, 5753 (2002).

12. A. I. Busev, , V. G. Tiptsova and V. M. Ivanov, *Handbook of the Analytical Chemistry of Rare Elements*, p. 78, Ann Arbor - Humphrey Science Publishers, London (1970).
13. E. P. Aleksandrov, B. D. Vasin and S. P. Raspopin, in *Phys. Chem. Electrochem. Molten and Solid Electrolytes*, pt. 1, p. 80, Akad Nauk SSSR, Ural. Nauch. Tsentr, Sverdlovsk (1979) (in Russian).
14. L. E. Ivanovskii and V. N. Nekrasov, *Gases and Ionic Melts*, p. 106, Nauka, Moscow (1979) (in Russian).
15. E. A. Ukshe, L. S. Leonova and N. G. Bukun, in *Ionic Melts*, Yu. K. Delimarskii, Editor, Vol. 1, p. 21, Naukova Dumka, Kiev (1974) (in Russian).
16. M. Harrison and A. Jackson, in *Actinides-2005 Int. Conf. 4-8 July, 2005*, *Abstracts*, p. 141, Manchester (2005).